

IN THE JAPANESE PATENT OFFICE

TRIAL NO. 26872/95

AND

TRIAL NO. 26875/85

AFFIDAVIT OF HOWARD TENNENT



HOWARD TENNENT, being duly sworn, deposes and says:

1. I reside at 301 Chandler Mill Road, Kennett Square, Pennsylvania 19348.

2. I hold the degrees of B.S. and M.S. in Chemistry from Rensselaer Polytechnic Institute and hold a Ph.D. in Physical Chemistry from the University of Wisconsin.

3. I have been an invited lecturer at California Institute of Technology, Massachusetts Institute of Technology, Stanford University, University of Chicago, University of Wisconsin and University of California Los Angeles.

4. I have been a consultant to Hyperion Catalysis International, Inc., owner of Japanese Patent Nos. 1701869 and 1869277 since 1981.

5. I am the inventor in Japanese Patent Nos. 1701869 and 1869277.

6. I make this Affidavit in defense of Japanese Patent Nos. 1701869 and 1869277.

Qualifications in the Field of Carbon Fibers

7. I studied surface treatments, properties and uses of PAN-based carbon fibers at Hercules Incorporated from 1975-81. Since 1981 I have been a consultant on synthesis, properties, and uses of fibers at Hyperion Catalysis International.

Background of my Invention of the Carbon Fibrils of Japanese Patent No. 1701869 and 1869277

8. I have worked extensively in the production, characterization and analysis of carbon fibers since 1975.

I consider myself qualified as an expert in the field of these compositions of matter.

9. I submitted an affidavit in the file of Japanese Patent No. 1701869. I confirm the statements made therein.

10. Carbon fibers prepared by catalytic decomposition of carbon-containing gases at metal surfaces were found in a wide variety of morphologies and had diameters ranging from tens of angstroms (a few nm) to tens of microns (tens of thousands of nm). Mixtures of fibers of different morphologies were usually obtained, sometimes mixed with non-filamentous carbon. The fibers were frequently coated with poorly organized thermal carbon.

11. Oberlin, Endo and Koyama, C., Carbon 14: 133 (1976), made carbon fibers with diameters in the range of 0.1 to 80 microns (100 to 80,000 nm) containing a well ordered graphitic core surrounded by an overcoat of less organized thermal carbon. Annealing the fibers at 2,500°C - 3,000°C converted them to highly ordered graphitic carbon. Tibbetts (Appl. Phys. Lett. 42(8): 666 (1983)) made straight carbon fibers also containing a graphitic core surrounded by a coating of pyrolytic carbon.

12. It was understood that the graphitic core grew catalytically in length at constant diameter and that thermal carbon deposited on the growing core. It was also understood, e.g. by Oberlin, Endo and Koyama and by Tibbetts that the respective core growth and pyrolytic carbon deposition processes could not be separated "because they are statistically concomitant". Journal of Crystal Growth: 32:335 (1976), referred

to at col. 2, line 31 of the patent. Tibbetts in Appl. Phys. Lett. 42(8): 666 (1983) stated that these two mechanisms are "overlapping" and that he was unable to grow fibers free of pyrolytically deposited carbon.

13. In my opinion, under the conditions taught by these references, the core growth and pyrolytic carbon deposition processes cannot be separated because the relative rates of core growth initiation, core growth and deposition of pyrolytic carbon are not separately sufficiently controllable and take place more or less simultaneously as a batch of fibers is being formed.

14. Efforts to grow carbon fibers by catalytic decomposition of carbon-containing gases at metal surfaces before my invention typically resulted in the production of one or more of several distinct types of fibers. These included, in addition to the graphitic core/pyrolytic overcoated species, fishbone fibers and capsule chain fibers. These also may have included an overcoat of pyrolytic carbon. In my Affidavit submitted in Japanese Patent No. 1701869, pars. 5 et. seq. I described the different types of fibers and fiber morphologies known prior to my invention. These are discussed below.

15. Fishbone fibers contain layers of carbon atoms in nested, truncated cones. Each of these ordered layers has graphitic structure. The angle between the c-axis and the axis of the fiber is less than 90° , i.e. the graphitic layers are not parallel to the axis of the fiber. A fishbone fiber cannot be converted by annealing at high temperature to a fiber in which the graphitic layers are parallel to the axis of the fiber.

16. Capsule chain fibers grow when layers of carbon almost completely coat a metal catalyst particle as they are formed. Before the carbon capsule is closed completely the metal is extruded from it and a new coating grows. The process is repeated many times. The resulting fiber is a series of oval capsules joined end to end. The carbon layers are curved. The end of each capsule opposite the opening through which the metal particle was extruded forms a septum across the hollow core of the fiber. The fiber diameter is not constant, being larger at the center of each capsule and smallest where they are joined. Capsule chain fibers cannot be converted by annealing at high temperature into a fiber in which the graphitic domains are parallel to the axis of the fiber.

17. Endo, et al. produced fibers having diameters above 1μ (1,000 nm). See for example Photograph 1 of Exhibit A-1 which depicts fibers having a diameter of 5000 nm. These fibers contain cylinders of ordered carbon surrounded by an outer coating of pyrolytic carbon. Pyrolytic carbon (thermal carbon) consists of individual, slightly wrinkled, graphitic layers which are very small (a few nm across) which are approximately parallel to their immediate neighbors but with little longer range order. When deposited on carbon fibers, these planes are oriented roughly parallel to the fiber axis. When the fibers were annealed at 2,500°C to 3,000°C the disordered carbon was converted into a more orderly, graphitic structure.

18. Annealing processes, have been used to convert certain disordered structures in as-grown fibers to more ordered

structures. While annealing is effective to cure defects and dislocations in as-grown crystal structures, when the graphitic domains are larger than a few nanometers, gross structural rearrangements are not possible because the energy required to break enough bonds simultaneously is too high. It is not possible to convert fishbone fibers or capsule chain fibers to fibers having carbon planes parallel to the fibril axis by annealing because the domains are too large. Lattice defects or bends in the carbon planes or misorientation of domains can be corrected.

19. It is possible to convert disordered, pyrolytic carbon to graphitic domains that are parallel to the fiber axis by annealing. In such processes, the carbon lattices surrounding the core of a fiber assume a polygonal configuration rather than the concentric rings of the fibrils of my invention. It is not possible to convert a kinky fiber into a straight fiber. Curved fibrils do not become straight when annealed. Distinct bends and kinks form which reduce the tensile strength of the fiber.

20. I am not aware of any carbon fiber grown before my invention which had the unique geometry and morphology of the fibrils described in my patent. I am not aware of any method for growing these unique fibrils directly or by annealing known before my invention.

The Invention

21. I was seeking ways to produce carbon fibers of smaller diameter having favorable performance properties. Carbon fibers are prized for their high conductivity, connectivity and

surface area. I wanted to increase the length to weight ratio of fibers because in doing so I would thereby also increase the performance to weight ratio of the fiber, i.e. conductivity, connectivity and surface area per unit weight of fiber.

22. As fiber diameters decrease, surface and total length per unit weight (or volume) of fibers increase. This is advantageous in a network of fibers, because as the total length of fibers increases, the distances between fibers in the network decrease and the number of fiber-fiber contacts increases. This leads to improved stiffness, toughness and electrical conductivity per unit weight of fiber. High surface is useful for fiber/matrix bonding in composites, and for catalyst supports, adsorbents and impingement filters.

23. I achieved these goals with the patented fibril of Patent No. 1701869 which is thin (3.5 to 70 nm), uniform (in cross-section), cylindrical, straight, long ($L/D > 100$) and has a graphite-like arrangement of carbon atoms. I also achieved these goals with the patented fibril of Patent No. 1869277 which is identical to that of Patent No. 1701869 except that the L/D ratio is from 5 to 100.

24. The advantage of smaller diameter fibers over larger diameter fibers is that the smaller diameter fibers have a higher length per unit weight. That leads to higher conductivity, connectivity and surface area per unit weight of fibers.

25. High length to diameter ratio improves the mechanical reinforcing properties and conductive properties of

the fibers within a host composition. In an interpenetrating network of fibers, as total length increases, the distances between fibers decrease and the number of fiber-fiber contacts increase. This improves stiffness, toughness and electrical conductivity per unit weight.

26. Uniform cross-section is important because variations in the thickness of the fibers due to defects in the structure contribute to poor performance. This has been established by recent tests conducted by Lieber, et al. ^{Science 212, 523 (1996)} (cite) who have shown that the highest points of electrical resistance in a fiber were located at its defects. Carbon in the non-uniform, "excess" part of the structure is wasted because it does not contribute to the performance of the fiber.

27. The graphite structure of carbon has the greatest tensile strength and the greatest conductivity. Accordingly, the greater the degree to which the carbon is ordered into graphitic domains, the greater will be its strength and conductivity per unit weight.

28. Straightness is an important feature of the patented fibril. The greater the straightness of the fibril, the higher its tensile strength and the more valuable it is as a reinforcing and conductivity enhancing additive to various polymers. Bends and kinks in prior art fibers lower the tensile strength of the fiber.

29. Pyrolytic carbon has significantly lower tensile strength and conductivity than ordered carbon in graphitic domains. Pyrolytic carbon does not contribute as much to tensile

strength or conductivity performance and represents less desirable carbon in the fiber.

Observation of the Prior Art
Cited by Demander in Trial No. 26872/95

Exhibit A-1. Photographs 1-4

30. I note the argument in the Demand that since the carbon planes in the core regions of the fiber appear to be ordered, that one could predict that a smaller diameter fiber (one in the diameter range of the patented fibrils) would have the completely ordered structure of the patented fibrils.

31. I stated above that it was widely accepted that the two processes of catalytic core growth and thermal carbon deposition could not be separated and that deposition of thermal carbon on the core of a vapor grown fiber was inevitable and unavoidable. In my opinion, it is scientifically unacceptable to focus on only a portion of the reference fiber structure (the portion around the hollow core) and then predict that only that portion of the structure could have been made. Such a small diameter fiber produced by prior art processes might have a completely different structure, e.g. a fishbone structure or a capsule chain structure and either of these might have an outer layer of pyrolytic carbon.

32. Prior art vapor grown carbon fibers of small diameter (less than 70 nm) had uneven, spindle shaped deposits of pyrolytic carbon laid down upon their core structure and were therefore both irregular in structure and non-uniform in diameter. This non-uniformity persisted after annealing. If the

process of fiber growth were permitted to continue, as for example in Exhibit A-1, the layer of pyrolytic carbon would become less spindle-like and more uniform. At the point the layer became substantially uniform, the diameter of the fibril would be many times greater than 70 nm, the largest diameter patented fibril.

33. Even if, for argument's sake only, a 3.5-70 nm fiber were to have been grown with a uniform carbon overcoat, upon annealing it would form a fiber with a polygonal cross-section. It would not be a patented fibril having a circular cross-section.

Exhibit A-1, Photograph 8

34. I believe that the fiber shown has either a capsule chain or a fishbone morphology. I see no evidence that it has the carbon atom arrangement which is critical in my patented fibril. I note that the fiber is kinked, not straight, and has a non-uniform diameter, and many septa. It is not clear whether it has a pyrolytic carbon overcoat. The fiber of Photograph 8 could not be straightened upon annealing and the carbon atoms would not rearrange to the graphite-like structure of the patented fibril.

Exhibit A-2

35. I note that no information is given with respect to the morphology of the fibers produced, whether they are straight or not, whether their cross-sections are cylindrical and uniform or whether they have a distinct inner core region.

Nothing in the reference which would suggest the geometry or the morphology of the patented fibril.

36. In my experience fluid bed processes make larger diameter fibers, i.e., above 70 nm. A process for producing fibers using a gaseous organic transition metal compound is very different from my process which employs ultrafine particles of a supported catalyst. In my opinion it is impossible to predict what processes might take place in the fluid bed process of Exhibit A-2 or what kinds of fibers might be produced.

Exhibit A-5

37. The sole example of fiber production describes a fiber having a diameter of 200 nm. The as-grown fiber has an ordered core and layers of thermal carbon. Even after heat treatment at 2900°C or above, the fiber contained a substantial amount of pyrolytic carbon. This does not suggest my invention.

Exhibit A-7

38. I note that the fibers produced are short and dendritic and that no other information (geometry, carbon atom arrangement, etc.) is given about their structure. The method is very different from my method.

Observations of the Prior Art
Cited by Demander in Trial No. 26875/95

Exhibit A-1

39. See pars. 30-36, above.

Exhibit A-3

40. The text on p. 229 of the reference discusses the characteristics of the fiber strands prepared by vapor growth.

the length will be 500 nm (5×10^{-4} mm). This will require a growth time of 0.0006 to 0.03 seconds. The reaction conditions described in Exhibit A-5 are nearly the same as in Exhibit A-3. It is obviously impossible to achieve initiation of fiber growth on a catalyst particle and then cause the fiber to stop growing in such a very short time.

45. For the reason stated above, the prior art of Exhibit A-3 does not suggest or lead in any way to my invention.

Exhibit A-4

46. See pars. 35 and 36, above.

Exhibit A-5

47. Exhibit A-5 describes a process in which a gaseous organometallic compound, e.g. ferrocene, is used as a source of the catalyst and wherein the reaction takes place in the gas phase. In this respect, the reference process is similar to that described in Exhibit A-5 in Trial No. 26872/95 discussed above in par. 37.

48. I further note that Example 1 discloses a fiber having a diameter of 200 nm which is nearly three times the diameter of the largest claimed fibril. The other examples do not disclose the diameter of the fibers formed.

49. I also note that no information is given about the morphology of the fiber, its uniformity, its straightness or its cross section. For all these reasons, the reference does not suggest the fibril of my invention.

The text describes a hollow tube, the wall of which is comprised of:

. . . long, straight, and monocrystalline carbon-layer surfaces, as seen in Fig. 5(c). The carbon-layer surfaces do not exhibit the three-dimensional graphite structure, but have turbostratic structures. . . . It is obvious that each fiber consists of two different structures; . . . The fine fiber strands [comprising] the hollow tube . . . followed by a thermal decomposition process (thickness growth process by CVD).

41. Fig. 5 shows a portion of a vapor grown carbon fiber comprising a hollow core, an ordered carbon structure around the wall of the hollow tube and an outer structure of thermally decomposed carbon. This is also shown in parts (b) and (c) of Fig. 5. The diameter of the fiber shown is in the order of 1200 Å (120 nm), nearly twice the largest diameter of the patented fibrils.

42. The vapor grown carbon fiber of Fig. 13 is not uniform in diameter. Still further, I note that the fiber does not appear to be straight. The fiber appears to have a pyrolytic carbon overcoat.

43. I note Demanders argument that the fiber made in the reaction process of Exhibit A-3, if taken out of the reaction zone timely, will not contain thermally decomposed carbon overcoat and that if there is some, the amount would be small. I disagree with that argument.

44. In Exhibit A-3, core growth rates of 1-50 mm/minute in the direction of growth are taught. For a final fibril diameter of 10 nm and a length to diameter ratio of 50,

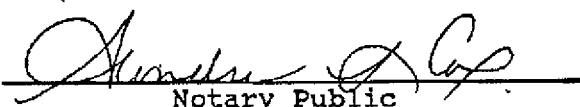
Exhibit A-6

50. See par. 37, above.

Further, deponent sayeth not.


HOWARD TENNENT

Sworn to and subscribed before me on
the 14th day of October, 1996.


Notary Public

